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EVALUATION OF THE ABSORPTION AND DESORPTION OF BIS(2-CHLOROETHYL) SULFIDE (HD) FROM WOOD SAMPLES

Eugene L. Vickers
Anthony F. Zirnhelt
Anthony Lofton
Larry M. Sturdivan
Foy E. Ferguson

RESEARCH DIRECTORATE

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Aberdeen Proving Ground, Maryland 21010-5423

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Vickers, Eugene L., Zirnhelt, Anthony F., Lofton, Anthony, Sturdivan, Larry M., and Ferguson, Foy E.

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The Research Directorate of the U.S. Army Chemical Research, Development and Engineering Center tested treated and untreated wooden samples submitted by the U.S. Forest Products Laboratory at the request of the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ to determine whether the wood samples met the U.S. Army NBC decontaminability requirements (upper limit of desorbed HD of 36 micrograms per square centimeter specified in MIL-C-46168C). Wooden samples representing 51 different treatments were submitted for analysis. Forty treatments grossly failed and were eliminated. The remaining 11 treatments were tested by covering a 3-cm² area of the surface with 25 microliters of HD (97% pure). To isolate the influences of wood type and their treatment from extraneous effects produced by different paths through the equipment, and the sequence in which the samples were tested, a statistically based experimental design was employed. Steel panels sprayed with aliphatic polyurethane served as controls. The results show that none of the wood samples met the acceptance criteria of MIL-C-46168C. Even the best treatment was more than double the 36 micrograms per square centimeter requirement.

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PREFACE

The work described in this report was authorized under U.S. Army - Funded Agreement No. FP-88 1050. This testing was started in April 1988 and was completed in June 1990. Due to test facility shut down, testing was postponed from late calendar year 1989 to early calendar year 1990.

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EVALUATION OF THE ABSORPTION AND DESORPTION OF BIS(2-CHLOROETHYL) SULFIDE (HD) FROM WOOD SAMPLES

1. INTRODUCTION

The U.S. Army requires that mission essential materiel meet Department of Defense standards for chemical survivability. The basic requirement is that select materials, if exposed to chemical agent, not retain the chemical agent in amounts which can cause subsequent harm to personnel. The overall objective of the work described in this report was to determine the amount of agent that was desorbed, under typical conditions over a 24-hour period, from various woods, wood composites and treated wood. This study was conducted in response to a request by the U.S. Forest Products Laboratory US(FPL) to the Project Manager, Ammunition Logistics, and performed by the Analytical Systems Group of the Research Directorate of the U.S. Army Chemical Research, Development and Engineering Center (CRDEC). This investigation is to establish whether or not these wood-based materials meet the standard for chemical survivability. CRDEC tested a number of types of treated and untreated materiels to ascertain their resistance to the absorption and subsequent desorption of toxic chemical agents. The test used was adapted from the procedure described in MIL-C-46168C (ME), used to evaluate Chemical Agent Resistant Coating (CARC). The test was modified as required to accommodate the automated monitoring equipment. According to the MIL standard, the upper limit on desorbed HD is 180 micrograms from a 5 square centimeter test area over a 24-hour period. This translates to 36 micrograms per square centimeter.

Wood samples submitted by US(FPL) had first been screened by exposure to chloroethyl ethyl sulfide (CEES), a simulant of the chemical agent, bis (2 chloroethyl) sulfide (HD). Some of the preliminary results were confirmed at CRDEC before agent testing was begun. The number of types of wood samples to be tested was reduced via a series of screening tests to eliminate those treatments desorbing large quantities of chemical agent. The test incorporated some of the best treatments from the screening tests along with samples which had been given those or other, similar treatments, then subjected to "rough handling" to simulate the wear and tear that wood products might experience on the battlefield. The experimental design for the test was chosen to statistically isolate the effect of the treatments that were applied to the wood samples from extraneous effects resulting from different paths through the equipment and the sequence in which the samples were tested. Samples of standard, primed metal panels, sprayed with an aliphatic polyurethane coating by the Belvoir Research, Development and Engineering Center were also inserted into the test as controls. These controls were determined to desorb approximately 3 times the allowable quantity of HD through tests conducted at Dugway Proving Ground according to MIL-C-46168C.

2. MATERIALS

A Chemical Agent Standard Analytical Reference Material (CASARM) distilled mustard (HD) from lot number HD-U-6216-CTF-N was used to test the wood samples. The mole percent purity was determined to be 97.6% by freezing point determination and 96.6% by Nuclear Magnetic Resonance (NMR). Major impurities were fragments of dithiane (1.5 mole %), ethyl (0.8 mole %), and ethylene (1.1 mole %) as determined from NMR spectra. This composition is typical of U.S. stock mustard.

Wood samples, as provided by the U.S. Forest Products Laboratory (FPL), consisted of Southern Pine, Aspen, Red Oak, Douglas Fir, Soft Maple, Hard Maple, and Waferboard Brand composite. Most of the samples tested were either coated with existing materials expected to enhance resistance to chemical agent or left uncoated. The samples were in one of two shapes: round disks with grooves cut in them to fit inside the test cell or squares. A listing of the samples tested along with details of treatment can be found in the Appendix. The wood samples were first screened by the US(FPL) using chloroethyl ethyl sulfide (CEES), a simulant much less toxic than mustard. A portion of the 51 samples which passed these simulant tests were also tested with the same simulant at CRDEC. The simulant-screening results from the two laboratories were in agreement.

3. EXPERIMENTAL PROCEDURE

As mentioned above, a modified CARC testing procedure was used for this study. The surface of the material being evaluated was covered with agent HD and allowed to remain covered for 30 minutes. The surface was then rinsed with solvent to remove any liquid agent and monitored for 24 hours to measure the agent desorbed from the surface.

3.1 Equipment.

A Telos Labs model 650-SP sulfur/phosphorus monitoring system was used to monitor the samples for mustard vapor in the form of sulfur emission. The monitoring system (manufactured by Telos Labs. Inc., Fremont, CA) is a multiport chemical analyzer which can sample up to 24 different sampling ports. A flame photometric detector was used to detect sulfur containing compounds. Two stainless steel blocks, each containing 5 sample cells, were connected to the monitoring system using teflon tubing. Thus, a total of 10 samples could be tested at one time. The Telos instrument was attached to the house vacuum which pulled air through the cells along with any agent vapor present into the instrument. Each cell was sampled for 37.5 seconds every 15 minutes. For the remainder of the interval the effluent airstream was directed through a charcoal adsorbent bed.

3.2 Experimental Design.

The experimental design used in the test was a Partially Balanced Incomplete Block (PBIB). This design is shown in the matrix given in Table 1. Three of the "best" treatments (code #327, 331 and 333) obtained from the screening runs were chosen for the test, along with some which had received similar coatings then subjected to "rough handling" before being submitted to CRDEC for testing. Interspersed among the treatments being tested were four groups of the control polyurethane-coated steel panels. The polyurethane coated control was known to exceed the required acceptance limit for HD desorption by a factor of almost three from previous tests at the Chemical Laboratory, Dugway Proving Ground. The polyurethane coated control was known to exceed the required acceptance limit for HD desorption by a factor of almost three from previous tests at the Chemical Laboratory, Dugway Proving Ground. Table 2 shows the day the sample was tested and the test cell used. There are four samples numbered 1, four numbered 2, etc. For example, Code 331 (lot #2) was tested on Days 1,2,3, and 5 and was placed in cells 5,1,6 and 7 respectively.

Table 1. Sample Allocation for the Test

Lot	Treatment	Lot	Treatment
1	Code 327	9	Code 393.5
2	Code 331	10	Control
3	Code 333	11	Code 356.5
4	Code 331.5	12	Code 404.5
5	Code 333.5	13	Code 185.5
6	Control	14	Control
7	Code 334.5	15	Control
8	Code 375.5		

NOTE: See the Appendix for description of Codes

Table 2. Sample Matrix for Test (lot numbers appear under each day)

Cell #	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
1	1	2	3	10	14	15
2	4	1	5	15	13	9
3	14	13	8	6	7	1
4	10	9	11	1	6	12
5	2	11	13	5	8	10
6	15	12	2	8	4	6
7	5	14	9	12	2	7
8	3	5	6	7	15	11
9	8	4	14	11	9	3
10	12	7	4	3	10	13

3.3 Procedures.

The monitoring system was calibrated daily by introducing certified, known concentrations of sulfur dioxide directly to the detector. The concentration of the calibration gas was changed by varying the flow of diluent air. During calibration a conversion factor table was generated and stored in the computer memory which translates the digital signal from the analyzer, expressed in analyzer response units (ARU), to parts per billion (ppb) concentration. The system's computer was programmed to convert the ppb concentration into micrograms per square centimeter of sample area.

Each combination of wood type and treatment was assigned a code number by the supplier. The various combinations (codes) will be referred to hereafter as "treatments" and the group of samples of each treatment will be referred to as "lots." The test contained 15 treatments which were tested together according to the experimental design. Four samples of each treatment (two round and two square) were tested except when samples were lost due to instrument malfunctions or when there were insufficient samples of a particular treatment to make up a full complement of four samples.

The procedure used during testing is described below:

a. Ten samples were randomly drawn from the lots selected according to the experimental design and placed on a stainless steel tray inside a fume hood.

b. 25 microliters of HD were dispensed from a disposable micro-pipette and spread over a 3 cm^2 area (in a circle 2 cm in diameter) in the center of each sample and left on the surface for 30 minutes.

c. After 30 minutes of contact time each sample was washed with agitation for 15 seconds in a sequence of two containers of isopropyl alcohol and a container of water, then allowed to air dry. The alcohol and water were replaced after each wash.

d. Finally, the samples were placed into individual sample cells and the air sampling process started.

4. RESULTS AND DISCUSSIONS

Predicted values for mustard desorbed were calculated from the raw data using an Analysis of Variance (ANOVA) technique. The predicted value of the mean desorption level for the treatment type as well as the lower 95% confidence limit on that mean is

included in Table 3. The desorption level of the control is significantly higher than the known values for those panels.

The confidence level is usually used to indicate that the mean of some population would meet a criterion with the specified level of confidence (e.g., the upper confidence limit is below a specified maximum) and we will not accept a nominally acceptable estimate without a high degree of confidence that the "true" population mean is in the acceptable region. Here, however, the confidence limit shows just the opposite. The figures in the table indicate that the upper limit on desorption is exceeded with a high measure of probability; i.e., there is less than a 5% chance that the "true" mean of any of the wood treatments is less than the limit established in the CARC specification.

Table 3. Results of Test

Code	HD Desorbed, micrograms/sq cm		
	Predicted Mean Amt.	Lower 95% Conf. Lt.	Pass/Fail
185.5	1,041	324	Fail
327	358	112	Fail
331	359	112	Fail
331.5	275	86	Fail
333	239	75	Fail
333.5	961	299	Fail
334.5	509	159	Fail
356.5	1,468	457	Fail
375.5	1,319	411	Fail
393.5	303	94	Fail
404.5	1,207	376	Fail
Control*	229	130	

*Control indicates the polyurethane coated steel panels.

5. CONCLUSIONS

This series of tests designed to ascertain the resistance of a number of types of treated wooden materials to chemical agents resulted in the following:

a. All samples failed the laboratory criterion of 36 micrograms per square centimeter.

b. The predicted mean desorption amount from the samples was greater than 100 micrograms per square centimeter.

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APPENDIX

Sample Description

Descriptions of samples used in the test are as follows:

Code	Sample	Wood	Treatment	Day
185.5	13	Red Oak	rough handled* + phenolic resin 761	2 3 5 6
327	1	Douglas Fir	Aromatic + aliphatic polyurethane coat	1 2 4 6
331	2	Red Oak	phenolic resin 761 + aliphatic polyurethane coat	1 2 3 5
331.5	4	Red Oak	rough handled phenolic resin 761 + aliphatic	1 2 3 5
333	3	Southern Pine	phenolic resin 761 + aliphatic polyurethane coat	1 3 4 6
333.5	5	Southern Pine	rough handled phenolic resin 761 + aliphatic	1 2 3 4
334.5	7	Red Oak	rough handled phenolic resin 875 + 2 aliphatic	2 4 5 6
356.5	11	Southern Pine	rough handled flame retardant + 2 aliphatic	2 3 4 6

375.5	8	Southern Pine	rough handled EHMA + fluoro	1 3 4 5
393.5	9	Hard Maple	rough handled phenolic resin 761	2 3 5 6
404.5	12	Waferboard 8% adh	rough handled + 2 aliphatic	1 2 4 6
Control	6	Steel panels	aliphatic polyurethane	3 4 5 6
Control	10	"		1 4 5 6
Control	14	"		1 2 3 5
Control	15	"		1 4 5 6

*The rough handled samples were supplied by Virginia Polytechnic Institute after being subjected to a rough handling treatment.

APPENDIX